# Factors Affecting the Crevice Corrosion Susceptibility of Alloy 22

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ABSTRACT

The susceptibility or Alloy 22 (N06022) to crevice corrosion may depend on environmental or external factors and metallurgical or internal factors. Some of the most important environmental factors are chloride concentration, inhibitors, temperature and potential. The presence of a weld seam or second phase precipitation in the alloy are classified as internal factors. The localized corrosion resistance of Alloy 22 has been extensively investigated in the last five years, however not all affecting factors were considered in the studies. This paper discusses the current findings regarding the effect of many of these variables on the susceptibility (or resistance) of Alloy 22 to crevice corrosion. The effect of variables such as temperature, chloride concentration and nitrate are rather well understood. However there are only limited or no data regarding effect of other factors such as pH, other inhibitive or deleterious species and type of crevicing material and crevice geometry. There are contradictory results regarding the effect of metallurgical factors such as solution heat treatment.

Keywords: N06022, crevice corrosion, environmental factors, metallurgical factors, temperature, chloride, inhibitors

INTRODUCTION

Several corrosion resistant nickel-based families of alloys exist. These include commercially pure nickel (Ni) (e.g. Ni-200 or N02200), Ni-copper (Cu) alloys (e.g. Alloy 400 or N04400), Ni-molybdenum (Mo) alloys (e.g. B-2 or N10665), Ni-Chromium (Cr)-Iron (Fe) alloys (e.g. Alloy 600 or N06600) and Ni-Cr-Mo alloys. [1] The family of Ni-Cr-Mo is rather large and continuously growing. They include alloys such as such as C-4 (N06455), C-276 (N10276), C-2000 (N06200), 59 (N06059) and 686 (N06686). [1,2] Alloy 22 belongs to the Ni-Cr-Mo family of nickel based alloys and contains nominally 22% Chromium (Cr), 13% Molybdenum (Mo) and 3% tungsten (W). [2] The Ni-Cr-Mo alloys were designed to withstand the most aggressive industrial applications, including reducing acids such as hydrochloric and oxidizing acids such as nitric. Chromium is the beneficial alloying element added for

protection against oxidizing conditions and molybdenum is the beneficial alloying element to protect against reducing conditions. [1,3-4] The base element (nickel) protects the alloy against caustic conditions. [1,3-4] All three elements, Ni, Cr and Mo act synergistically to provide resistance to environmentally assisted cracking in hot concentrated chloride solutions. [1,3-4] The alloying elements Cr and Mo also provide resistance to localized corrosion such as pitting and crevice corrosion in chloride containing solutions. Some of the Ni-Cr-Mo alloys also contain a small amount of tungsten (W), which may act in a similar way as Mo regarding protection against localized corrosion. [5] Ni-Cr-Mo alloys are practically immune to pitting corrosion but they may suffer crevice corrosion under aggressive environmental conditions.

## RESISTANCE OF ALLOY 22 TO LOCALIZED CORROSION IN INDUSTRIAL APPLICATIONS

For an engineering alloy selection process in an industrial application, many times the pitting equivalent ratio (PRE) criteria is applied to rank Ni-Cr-Mo alloys (and stainless steels). [5-7] The higher the PRE the higher the resistance of the alloy to localized corrosion. Alloy 22 has one of the highest PRE numbers for nickel based alloys and therefore is one of the most resistant engineering alloys to localized corrosion. [3,5,8] For example, due to its balanced content of Cr and Mo, Alloy 22 has been selected to fabricate a large flue-gas desulfurization (FGD) plant in a coal-fired power station in the United Kingdom. [9] This plant neutralizes over 250,000 tons of sulfur a year that otherwise would end up in the atmosphere. In this FGD treatment plant the hot gases enter the system at a temperature of 130°C, then a limestone slurry is sprayed down through the gases in the absorber. [9] The clean gases are released to the atmosphere at 80°C. [9] Within the absorber, a calcium chloride solution is formed due to the reaction between the chlorine from the coal and the calcium from the limestone (calcium carbonate). [9] The concentration of chloride was estimated to be 30,000 ppm (3% or approximately 1 M Cl⁻). A by-product of the operation of this plant is the production of high quality gypsum (calcium sulfate). It has been reported that after more than ten years in service, the Alloy 22 structure has not suffered any type of corrosion degradation. [10]

Due to its excellent resistance to general and localized corrosion, Alloy 22 was also selected for the fabrication of the outer shell of the high level nuclear waste containers for the proposed Yucca Mountain repository. [11-12]

## TESTING FOR CREVICE CORROSION IN THE LABORATORY

There are several methods to determine the susceptibility of Alloy 22 and other engineering alloys to crevice corrosion. [13-14] These methods can be divided into immersion tests and electrochemical tests. In both types of tests the alloys are driven to the limit of resistance to localized corrosion by changing the environmental variables including chloride concentration, temperature and applied potential. That is, each alloy is characterized by, for example, the maximum temperature it can tolerate without undergoing localized corrosion at a constant chloride concentration and at a constant applied potential. Immersion tests are generally used to assess critical crevice temperatures, for example in standard ASTM solutions. [1,6,13] There are no universal or single methods for measuring crevice corrosion susceptibility of an engineering alloy. Each method provides a different parameter to compare, for example, the behavior of one alloy with another in a fixed environment or for one alloy to compare one electrolyte with another. The most popular testing methods were written into ASTM standards but other commonly accepted methods do not have a specific standard.

Alloy 22 was mostly tested to obtain critical potentials such as crevice repassivation potentials. [8,14-26] The most common test used for Alloy 22 was the cyclic potentiodynamic polarization (CPP)

or ASTM G 61. [13] Other typical tests are the Tsujikawa-Hisamatsu Electrochemical (THE) method and the constant potential or potentiostatic (POT) test, which do not have ASTM standards. [14-15] Other researchers used variations of the THE and CPP methods (mixed) by applying one potentiodynamic scan rate in the forward direction a potentiostatic hold in the middle and another potentiodynamic scan rate in the reverse direction. [25] Regardless of all the combinations or variations of the electrochemical test methods (CPP, THE, POT and mixed), the values of repassivation potential for Alloy 22 seem comparable. [15] This finding suggests that the crevice repassivation potential is a property of the alloy in each testing condition and does not depend greatly in the manner it is obtained.

## FACTORS INFLUENCING CREVICE CORROSION OF ALLOY 22

Alloy 22 can be considered not susceptible to pitting corrosion in practical applications in chloride containing environments. However, Alloy 22 may be prone to crevice corrosion in certain conditions. There are many factors or variables that influence the susceptibility (or resistance) of Alloy 22 to crevice corrosion. They can be classified into environmental or external factors and metallurgical or internal factors. External factors include:
   a. Chloride Concentration
   b. Temperature
   c. Applied Potential
   d. Presence of inhibitors such as nitrate, sulfate and carbonate
   e. Presence of other deleterious species such as fluoride and bromide
   f. Proton activity (pH)
   g. Microbial activity, organic acids, etc.
   h. Crevice former geometry (tightness of the crevice)
   i. Type of crevicing material, etc.

Internal factors are related to the metallurgical condition or characteristic microstructure of the part fabricated using Alloy 22. The following questions should be considered when assessing the influence of internal factors
   1. Is the alloy in the mill-annealed (MA) wrought condition?
   2. Is there a weld seam containing a cast or dendritic microstructure?
   3. Was the alloy solution heat-treated (SHT)? At what time and temperature?
   4. Was the alloy black annealed or bright annealed?
   5. Is the SHT film present in the surface of the alloy?
   6. Was the material thermally aged? At what time and temperature? Etc.

Each one of these factors, external and internal affect the susceptibility of Alloy 22 to crevice corrosion in a given manner, considering that all the other factors remain unchanged. Many of these factors (such as chloride concentration, inhibitor nitrate and temperature) have been studied in some detail; however, the influence of other factors such as nature of crevice former of crevice geometry still needs to be investigated.

Chloride Concentration

The chloride concentration has a significant effect on the resistance of Alloy 22 to crevice corrosion. As the chloride concentration increases, the susceptibility of Alloy 22 to crevice corrosion increases. At each testing condition, the susceptibility of Alloy 22 to crevice corrosion can be evaluated taking into consideration the value of the repassivation potential. When a cyclic potentiodynamic polari-

zation (CPP) test (ASTM G 61) [13] is performed, a hysteresis in the reverse potential scanning may indicate the presence of crevice corrosion. It is generally accepted that the potential at which the current density in the reverse scan reaches a value of 1 or 2 µA/cm² can be called the repassivation potential. [15-16] The repassivation potential can also be equated to the potential at which the reverse scan crosses the forward scan in the passive region of potentials. [20] For most of the published results the values of repassivation potential measured by either method (constant current density or crossover) using cyclic potentiodynamic polarization are similar. [14-16]

It has been shown for Alloy 22, that the repassivation potential decreases linearly as the chloride concentration increases logarithmically. [15-16] That is, the relationship between repassivation potential (ER) and chloride concentration has the following form (Equation 1)

$$ER = A - B \cdot \log[Cl^-] \qquad (1)$$

Where A and B are constants, which depend on the temperature and the other affecting variables.

Figure 1 shows the repassivation potential of Alloy 22 at 90°C from CPP curves as a function of chloride concentration for NaCl solutions. [15] The symbols represent the actual values of repassivation potentials both for as-welded (ASW) and mill-annealed (MA) specimens. There are two types of repassivation potentials plotted in Figure 1: [15] ER1, which is the repassivation potential to reach 1 µA/cm² in the reverse scan and ERCO, which is the repassivation potential for the cross over of reverse on forward scans. The lines represent logarithmic fits taking the points for both types of materials (ASW and MA). Figure 1 shows that there is a linear relationship by which the repassivation potential for Alloy 22 decreases as the logarithmic of the concentration of chloride ions increases. A similar finding was reported before. [27]

Temperature

Temperature of the electrolyte solution is one of the crucial factors controlling the susceptibility of Alloy 22 to crevice corrosion. It has been reported that there is approximately a linear reverse relationship between the repassivation potential and the temperature, that is, the repassivation potential decreases as the temperature increases. Evans et al. reported that in 5 M $CaCl_2$, as the temperature increased from 30°C to 120°C the repassivation potential for crevice corrosion decreased linearly from approximately 0 mV to -130 mV in the saturated silver chloride electrode scale (SSC), when using the testing method Tsujikawa-Hisamatsu Electrochemical (THE) (Figure 2). [15] However, when the CPP method was used, the repassivation potential was not linear with the temperature in the entire range of tested temperatures. [15] The repassivation potential (ER1) decreased rapidly from approximately 700 mV SSC at 30°C to approximately –120 mV SSC at 75°C (820 mV decrease in a 45°C interval) and, above 75°C, ER1 decreased more gradually to approximately –200 mV SSC at 120°C (80 mV decrease in the second 45°C interval) (Figure 2). [15] Dunn et al. reported that the repassivation potential for Alloy 22 in 1 M NaCl decreased from approximately +220 mV SCE (saturated calomel electrode) at 80°C to approximately -200 mV SCE at 150°C. [16] Similarly, in 4 M NaCl solution, the repassivation potential decreased from approximately +120 mV SCE at 80°C to approximately –200 mV SCE at 150°C. [16] That is, a different repassivation potential and temperature relationship was found for different chloride concentrations (1 M and 4 M). [16]

Potential

Applied potential is one of the four most important variables controlling the localized corrosion susceptibility of Alloy 22 (the other are chloride concentration, temperature and inhibitors – mainly nitrate). It is acknowledged that if the corrosion potential ($E_{corr}$) of Alloy 22 in certain conditions of for

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example chloride concentration and temperature is below the repassivation potential for crevice corrosion, the creviced alloy will not develop crevice corrosion. [20] However, if the conditions in the system are such that the $E_{corr}$ can be driven to the vicinity of the values of repassivation potentials or even higher, creviced Alloy 22 may develop crevice corrosion. Dunn et al. reported that the $E_{corr}$ of Alloy 22 in aerated 4 M NaCl at 95°C increased to up to –100 mV SCE for immersion times as long as 750 days. [16] However, after this exposure time the creviced specimen did not develop crevice corrosion. [16] According to the same authors, in 4 M NaCl at 95°C, the repassivation potential of Alloy 22 is approximately –30 mV SCE. [16] That is, the $E_{corr}$ was below the repassivation potential and therefore the alloy did not develop crevice corrosion. [20]

Evans et al. applied constant potentials to creviced Alloy 22 specimens in 5 M CaCl$_2$ at 120°C both below and above the repassivation potential in these conditions. [15] As expected, it was reported that specimens polarized below the repassivation potential remained passive for a week with current densities in the order of $10^{-8}$ A/cm²; however the specimen polarized above the repassivation potential developed crevice corrosion in a matter or hours (Figure 3). Therefore, the selection of the repassivation potential (ER) as a critical potential (E$_{crit}$) below which Alloy 22 would not suffer crevice corrosion is a valid criteria for modeling potential drift effects (ennoblement of $E_{corr}$). [20]

Inhibitors of Localized Corrosion (Nitrate, Sulfate and Carbonate)

Oxyanions such as nitrate ($NO_3^-$), sulfate ($SO_4^=$) and carbonate ($CO_3^=$) act as inhibitors for localized corrosion of Alloy 22 in chloride containing solutions. [12,17-27] That is, the alloy is less susceptible to crevice corrosion in a chloride solution containing the oxyanions than in a pure chloride solution of the same concentration. Figure 4 shows the effect of increasing amount of nitrate ions on the repassivation potential of Alloy 22 in 1 m NaCl solution at 60°C, 80°C and 100°C. Figure 5 shows a similar graph for 6 m NaCl base electrolyte. [A] The amount of nitrate in Figures 4 and 5 were added so the ratio of nitrate to chloride remained the same at 0.05, 0.15 and 0.5. [19] Both in 1 m NaCl and 6 m NaCl, at a nitrate to chloride ratio of 0.15 Alloy 22 shows repassivation potentials higher than 200 mV SSC at 60°C and 80°C. When the repassivation potential is higher than approximately 200 mV SSC, the tested specimens did not show typical crystalline crevice corrosion (Type I). At 100°C, the ratio of nitrate to chloride needed for inhibition of crevice corrosion appears to be between 0.15 and 0.5. Figures 4 and 5 seem to suggest that the total chloride concentration was not important for the resistance of Alloy 22 to crevice corrosion provided the ratio of nitrate to chloride remained higher than 0.15. However, Ilevbare et al. reported that the critical ratio of inhibitor seems to be temperature dependent. [19]

Inhibition of crevice corrosion only occurs above a critical oxyanion to chloride ratio. [18-20,23,25] For example, for nitrate ions, the critical ratio was determined to be 0.2 for 0.5 M NaCl at 95°C. [18,23] It has been shown that the critical nitrate to chloride ratio depends on the temperature but may not be a strong function of the total chloride concentration. [19] Other authors expressed that this critical nitrate to chloride ratio is not strongly dependent on the total chloride concentration and temperature. [25] Dunn et al. determined that for MA Alloy 22 in a 4 M MgCl$_2$ solution the critical nitrate to chloride ratio was 0.1 at 80°C and 0.15 at 110°C. [25] Similarly, Dunn et al. determined that the in a 0.5 M NaCl solution at 95°C, the critical carbonate to chloride ratio was 0.05 and the critical bicarbonate ($HCO_3^-$) to chloride ratio was 0.2. [25] Dunn et al. also reported that sulfate ions inhibited crevice corrosion of thermally aged (5 min at 870°C) Alloy 22 in 0.5 M NaCl at 95°C for sulfate to chloride ratios of 0.1, 0.2, 0.3, 0.4 and 0.6. Under these tested conditions the repassivation potentials were generally +200 mV SCE and higher. [25]

Ilevbare tested the resistance to crevice corrosion of MA multiple crevice assemblies (MCA) Alloy 22 specimens in 4 M NaCl and the effect of adding of 0.04 M and 0.4 M Na$_2$SO$_4$ in the temperature

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[A] Figures 4 and 5 were redrawn based on data from Reference 19.

range between 45°C and 105°C. [26] That is, the studied sulfate to chloride ratios were 0.01 and 0.1. [26] Figure 5 has been redrawn based on data in Reference 25. Figure 6 shows that the addition of 0.04 M and 0.4 M sulfate ions has an effect on the repassivation potential at 60°C, but only little effect at 75°C and higher temperatures. However, Ilevbare reported a beneficial effect of sulfate ions (especially at 0.4 M concentration) at all temperatures based on the appearance of the corrosion in the creviced areas. [26] Dunn et al. reported inhibition of short term thermally aged Alloy 22 at a ratio of sulfate to chloride of 0.1 (and higher) in a 0.5 M NaCl solution. [25] It could be that the slight difference in the results between Dunn et al. and Ilevbare is due to the total amount of base chloride and also to the different crevicing mechanism used for the tested specimens. [25,26]

Presence of other deleterious species such as fluoride and bromide

The effect of fluoride ($F^-$) and bromide ($Br^-$) ions on the corrosion behavior of Alloy 22 has not been as extensively investigated as the effect of chloride ($Cl^-$) ions. Prismatic Alloy 22 specimens (ASTM G 5) were tested in 1 M NaCl pH 6 and in 1 M NaF pH 9 solutions at 50°C. [28] The passive current density in both solutions was the same and approximately $2 \times 10^{-6}$ A/cm². The breakdown potential (E20) was 635 mV SCE in the chloride solution and 344 mV SCE in the fluoride solution. The difference in the breakdown potential can be mainly attributed to a difference in the pH of the electrolytes. The reversed CPP did not show hysteresis in either solution and the specimens did not suffer either pitting corrosion or crevice corrosion in any of these electrolytes, even after polarization to potentials higher than 800 mV. [28] Dunn et al. tested the influence of fluoride ions when added to 0.5 M NaCl solutions at 95°C for 5 min at 870°C thermally aged Alloy 22. [25] They reported that fluoride anion was not an inhibitor to crevice corrosion as found for nitrate, sulfate and carbonate oxyanions. [25]

Rodríguez et al. tested the corrosion susceptibility of MA and thermally aged Alloy 22 in 1 M NaF solutions at pH 6, 7.3 and 9. [29] Thermal aging was performed to create conditions of full aging with TCP phases (10 h at 760°C) and long range ordering (LRO or 1000 h at 538°C). Rodríguez et al. did not find localized corrosion (pttting or crevice corrosion) in any of the tested conditions even though the specimens were polarized to anodic potentials where current densities of up to 10 mA/cm² were applied. Small hystereses observed in the reverse CPP were attributed to uniform film dissolution in the metal. [29] Rodríguez et al. also performed electrochemical tests for Alloy 22 under the same metallurgical conditions in 1 M NaCl pH 2, 6 and 9 and 0.5 M NaCl + 0.5 M NaF at pH 6 and 9. [30] Comparing their results with the 1 M NaF results they concluded that Alloy 22 seemed more susceptible to crevice corrosion in the mixed salt solution than in the pure 1 M NaCl solution of the same pH. [29-30]

Limited studies exist on the effect of bromide ions on the localized corrosion susceptibility of Alloy 22. Cyclic potentiodynamic polarization (CPP) tests were carried out in 1 M NaCl and 1 M NaBr solutions at 50°C. [31] Both solutions had a similar pH of approximately 6. A slightly higher repassivation potential was reported for MA Alloy 22 in the bromide solution than in the chloride solution. However, under the tested conditions Alloy 22 did not suffer either crevice or pitting corrosion in neither solution. [31] It has also been reported alloying elements such as Mo, which are highly beneficial for protection against localized corrosion in chloride solutions may not be as efficient in bromide solutions. [31]

A more systematic study of the influence of fluoride and bromide on the repassivation potential of Alloy 22 is needed. This study should cover, for example, from trace amounts of fluoride to one to one fluoride to chloride ratios for varying base chloride concentrations.

Proton concentration (pH)

The crevice corrosion resistance of Alloy 22 was not studied in detail as a function of the proton activity (pH) of the electrolyte. Electrochemical tests were performed in electrolyte solutions of varying pH, from 2.8 for simulated acidified water (SAW) to pH ~ 13 for basic saturated water (BSW). Crevice

corrosion was never found for Alloy 22 in multi-ionic solutions simulating concentrated ground waters such as SAW and BSW using the cyclic potentiodynamic polarization (CPP), even after large anodic polarizations at temperatures near the boiling point of the electrolytes. Most of the repassivation potential results from electrochemical tests were obtained between pH 5 and 8, since this is the range of pH of most chloride-based salt solutions. Brossia et al. reported repassivation potentials at pH 6 and 8 as a function of the chloride concentration. [27] This was done for different types of Alloy 22 materials, so a comparison of the influence of pH is not possible. [27] The effect of pH is many times difficult to assess since other more important factors such as chloride concentration and temperature were also varied when the pH varied. Therefore, a clear impact of the pH value (keeping all other influencing variables constant) on the localized corrosion behavior of Alloy 22 still needs to be investigated in detail. It is likely that the pH would have more impact in values such as breakdown potentials (E20 or E200) than in repassivation potentials (such as ER1 or ERCO). For repassivation potentials the material would respond to its behavior in the aggressive solution (low pH) inside the crevice rather than on the pH value of the bulk solution. It is necessary to conduct a systematic study in which the repassivation potential of Alloy 22 will be assessed as a function of the pH, from example from 1 to 13, while maintaining all the other factors (chloride, temperature, metallurgical condition, etc.) constant.

Microbial Activity and Organic Acids

Microbial activity may alter the environment and therefore impact on the resistance of Alloy 22 to crevice corrosion. By one mechanism, fungi in the environment may produce organic acids such as propionic and oxalic acids. [32] It was found that oxalic acid even at the high concentration and temperature of 1 M at 90°C did not induce crevice corrosion in Alloy 22. [32] It still needs to be investigated the behavior of organic acids in presence of chloride ions and the oxyanions. In this study, the influence of the pH should be separated from the influence of the organic acids per se.

Crevice Former Nature and Geometry

Localized corrosion of Alloy 22 can be divided mainly into pitting corrosion and crevice corrosion. Pitting corrosion is rarely reported for Alloy 22, except for standard ASTM-type electrolytes. [1,6] Crevice corrosion was reported in most of the recent studies of localized corrosion of Alloy 22. Crevice corrosion is defined by ASTM as a type of localized corrosion that happens in a metal "at, or immediately adjacent to, an area that is shielded from full exposure to the environment because of close proximity between the metal and the surface of another material." (ASTM G 15) [13] NACE International also defines crevice corrosion similarly, "in which the site of attack is an area where free access to the surrounding environment is restricted." [33] The "restricting material" or "other material" could be another metal or a non-metal such as a organic gasket or deposits such as salts, corrosion products, oxides, dust, etc.

It is known from other materials (such as austenitic stainless steels) that the crevicing geometry or gap between the foreign material and the test specimen is very important for the susceptibility of the tested material to suffer crevice corrosion. The tighter the gap the easier crevice corrosion can be started. Most of the crevice corrosion studies for Alloy 22 carried in the laboratory involved the crevicing of the specimens with PTFE (polytetrafluoroethylene) washers [8,16,18,21-25,27] or ceramic washers that were coated with PTFE tape. [14-15,19-20,26,32] Different amount of loads (torque) were applied to the gaskets to ensure a tight crevice; however, the gap size has never been quantified. It is assumed that the crevicing mechanism of a ceramic washer coated in PTFE tape would be more demanding to the test specimen than a PTFE alone washer, since more pressure can be applied to the former and therefore develop a tighter gap. It still needs to be investigated what would be the critical gap size needed to nucleate crevice corrosion in Alloy 22 in a given environment when the crevicing material is a metal (such as another

Alloy 22 plate). Additionally, it should be investigated the susceptibility of Alloy 22 to crevice corrosion when crevice formers made of a pure ceramic material such as when a dust cake or a rock washer are used. It has been argued recently that a dust crevice former will not allow for sufficient oxygen depletion in order to create conditions for the nucleation and growth of crevice corrosion in Alloy 22. [34]

Internal Factors

Effect of internal factors on the resistance of Alloy 22 to crevice corrosion include differing metallurgical conditions of the material such as wrought mill-annealed (MA) vs. as-welded (ASW), solution heat treated (SHT) vs. ASW, MA vs. high temperature aged (HTA), etc. These factors are commonly grouped as "fabrication" factors. [35-36] Currently, contradictory results are available on the "fabrication" effect on the repassivation potential of Alloy 22. Some researchers reported that the behavior of MA and ASW materials were the same regarding resistance to crevice corrosion. [15] Other researchers reported that welded material was less resistant to localized corrosion than MA material. [35-36] They also reported that solution heat-treated (SHT) welds were less resistant to crevice corrosion than ASW material. [35-36] It has been attributed, for example, that the lower resistance of Alloy 22 to crevice corrosion in the SHT condition was due to the precipitation in the weld of topologically closed packed (TCP) phases. However, the lower potentials reported for the solution heat-treated materials (15 min. at 1125°C) [36] are still higher than the values reported for as-welded material by other researchers. [15] That is, the latter results are more conservative. It is likely that the crevicing mechanism used by Evans et al., [15] was more demanding to the specimen than the crevicing mechanism used by Dunn et al. [36] This may have resulted that the Evans et al. data [15] was less sensitive to microstructure than the Dunn et al. data. [36]


TYPES OF CORROSION ATTACK UNDER OCCLUDED CONDITIONS IN ALLOY 22

When creviced Alloy 22 specimens are polarized to relatively high anodic potentials in chloride containing environments at temperatures above ambient, two main types of attack may be induced under the crevice former. These occluded conditions corrosion modes are identified as Types I and II.

Type I of attack appears as a shiny crystalline area, under an optical microscope or even under the naked eye (Figure 7). This crystalline attack will appear under the crevice former of adjacent to it, depending on the solution composition or the testing method. [14] Depending on the extent of the attack, the grains of the alloy may be discernible and, with the help of scanning electron microscopy (SEM) even crystal planes within the grains are observable (Figure 8). This attack seems to progress following the lower energy planes in the crystal structure of the grains. In certain cases (sometimes depending on the mode the potential is applied) the attack under the crevice former will appear as intergranular corrosion or intergranular attack (IGA). [14] IGA is also observed in the creviced area when the alloy is in the thermally aged (HTA) condition. The same forms of attack (crystalline and intergranular corrosion) can also be obtained when a coupon of Alloy 22 is corroded in a boiling solution of hydrochloric acid (HCl). The crystallographic similarity of these modes of corrosion suggests that when Alloy 22 suffers Type I crevice corrosion under anodic polarization, a hydrochloric acid solution forms under the crevice former. Type I of crevice corrosion is considered the true crevice corrosion for Alloy 22. Figures 7 and 8 show images of specimen DEA3129, which was tested using CPP in 1 M NaCl at 90°C. The value of ER1 for DEA3129 was –51 mV SSC. [15] The CPP curve for specimen DEA3129 had a hysteresis loop in the reverse scan and ERCO was –24 mV SSC.

Type II of attack may also occurs under the crevice former but has a spotty dull gray appearance under the optical microscope. Type II is easy to differentiate from the crystalline shiny condition of Type I attack (Figure 9). Compare the Type I attack in Figure 7 (at 70 times magnification) with Type II attack in Figure 9 (at 100 times magnification). The difference in the extent of corrosion between these

two types is apparent. Under the SEM, Type II may show isolated shallow crystallographic etch pits (Figure 10). These etch pits are less than 5 µm diameter. Type II attack generally occurs when potentials above transpassivity are applied to the specimen in non-aggressive solutions (such as low concentration chloride or temperatures below 75°C). Under the naked eye or an optical microscope, the dull appearance of Type II attack may not be different from the transpassive dissolution occurring in the areas of the specimens outside the crevice former (boldly exposed to the solution). In Type II attack, the environment under the crevice former does not seem to reach the aggressive conditions (of low pH for example) necessary for crevice corrosion such as in Type I attack. The extent of Type II attack is not also important to produce a hysteresis loop in the CPP curve. Figures 9 and 10 show images of specimen DEA3181 tested using CPP in 5 M CaCl$_2$ at 60°C. [15] The value of ER1 for DEA3181 was 758 mV SSC. [15] This value is more than 800 mV higher than the ER1 for the specimen that produces Type I attack (Figures 7 and 8). The CPP curve for specimen DEA3181 did not have a hysteresis loop in the reverse scan. Therefore, Type II attack is not considered true crevice corrosion in Alloy 22.

## SUMMARY

1. Factors that affect the susceptibility of Alloy 22 to crevice corrosion can be grouped into external or environmental factors and into internal or metallurgical factors

2. The most important external factors are chloride concentration, temperature, applied potential and presence of inhibitive oxyanions

3. Internal factors are related to the various metallurgical conditions of the alloy, for example, welded vs. wrought, mill annealed vs. solution heat-treated

4. The relationship between the repassivation potential and the temperature or chloride concentration or presence of nitrate are currently understood

5. Other environmental factors such as proton activity, crevicing material and crevice geometry, presence of other inhibitive or detrimental species still need to be investigated

6. Contradictory information exists in the literature regarding the effect of internal factors in the repassivation potential of Alloy 22. More systematic research is needed in this field as well

7. Two types of attack under the crevice former during cyclic polarization have been identified. Only Type I is considered true crevice corrosion

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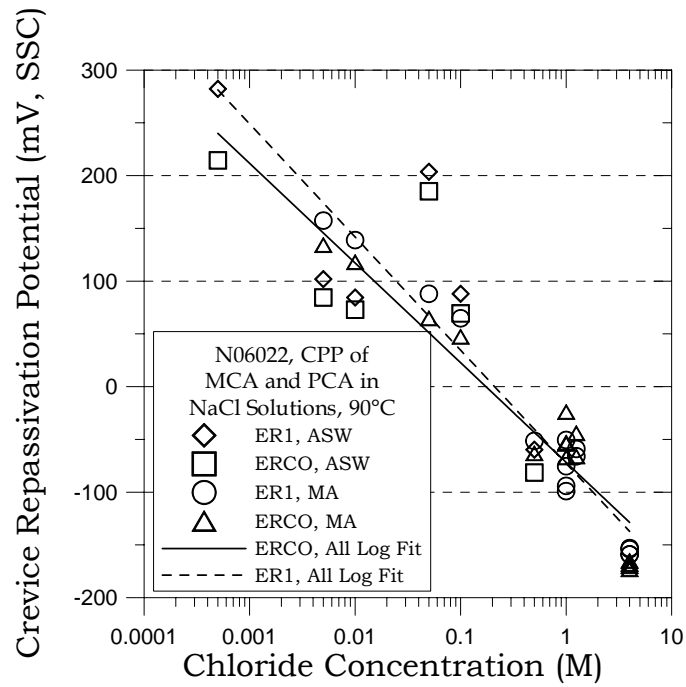
37.

FIGURE 1 – Repassivation potential for Alloy 22 at 90°C
as a function of chloride concentration for NaCl solutions
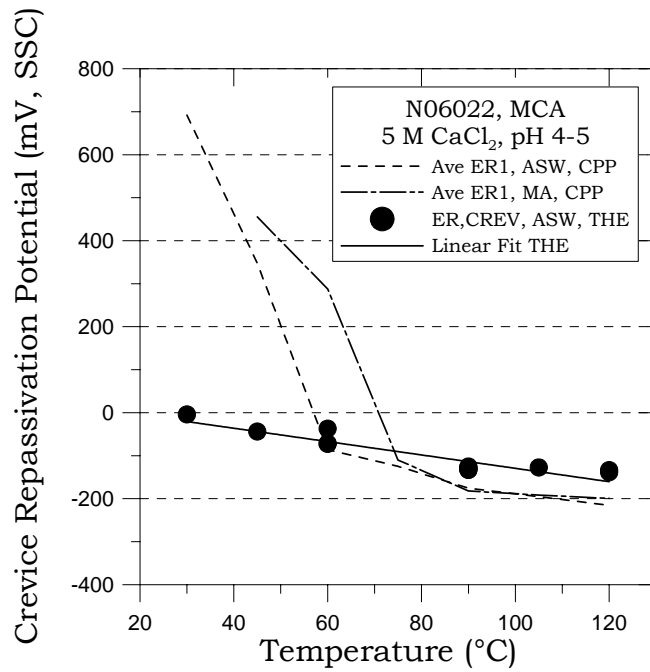


FIGURE 2 – Repassivation potential for Alloy 22 in 5 M CaCl$_2$
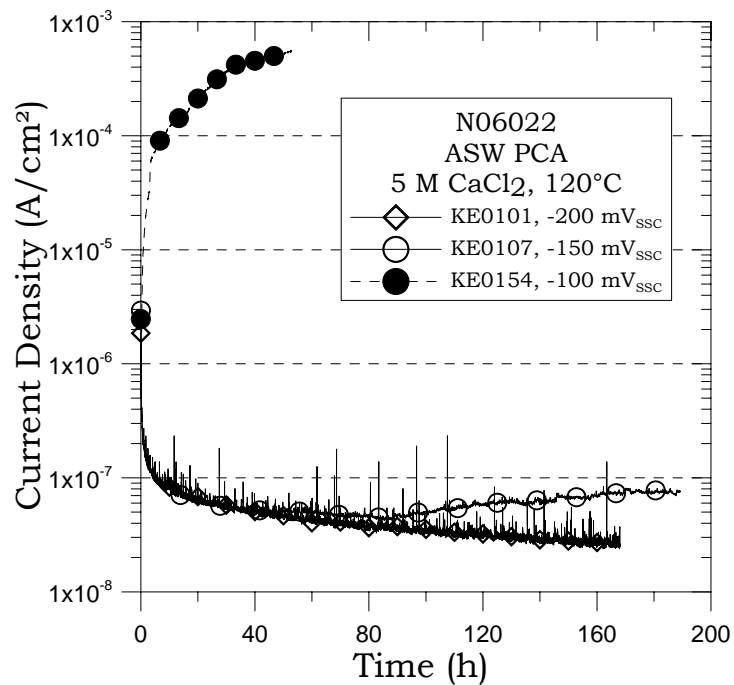as a function of electrolyte temperature

FIGURE 3 – Constant Potential tests for Alloy 22 in 5 M CaCl$_2$.
Crevice corrosion is initiated at E > ER (-130 mV SSC).



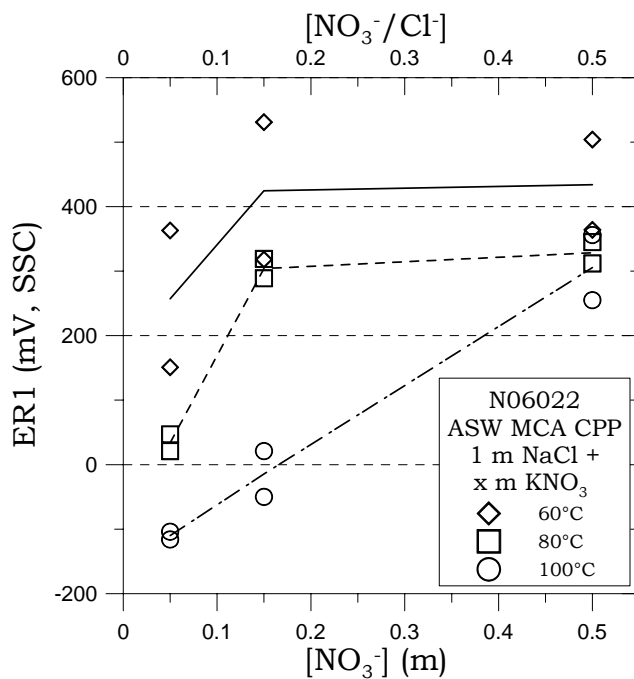FIGURE 4 – Repassivation potential for Alloy 22 at 60°C, 80°C and 100°C
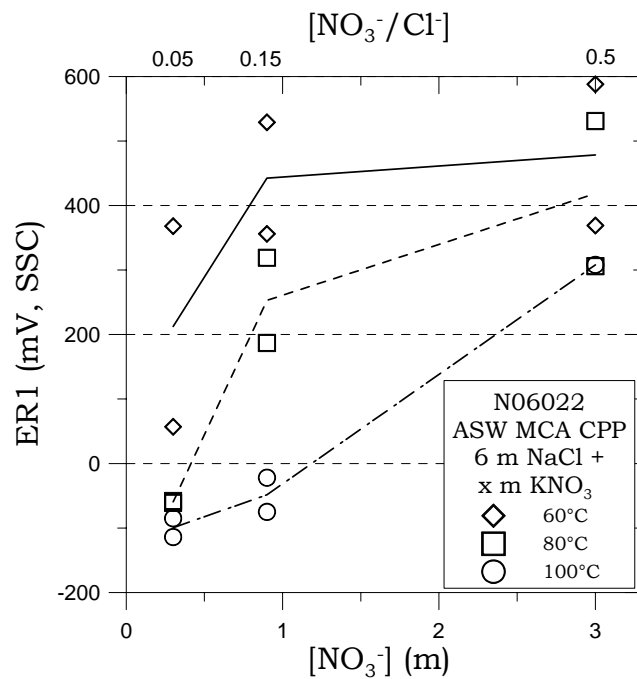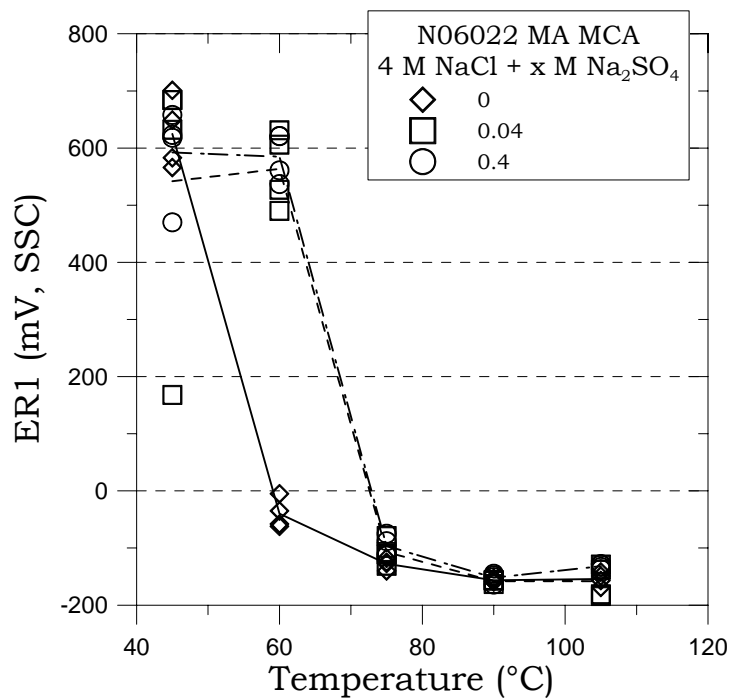in 1m NaCl with increasing additions of KNO$_3$. Data from Ref. 18

FIGURE 5 – Repassivation potential for Alloy 22 at 60°C, 80°C and 100°C
in 6m NaCl with increasing additions of KNO₃. Data from Ref. 18



FIGURE 6 – Repassivation potentials for Alloy 22 in 4 M NaCl solution as a function
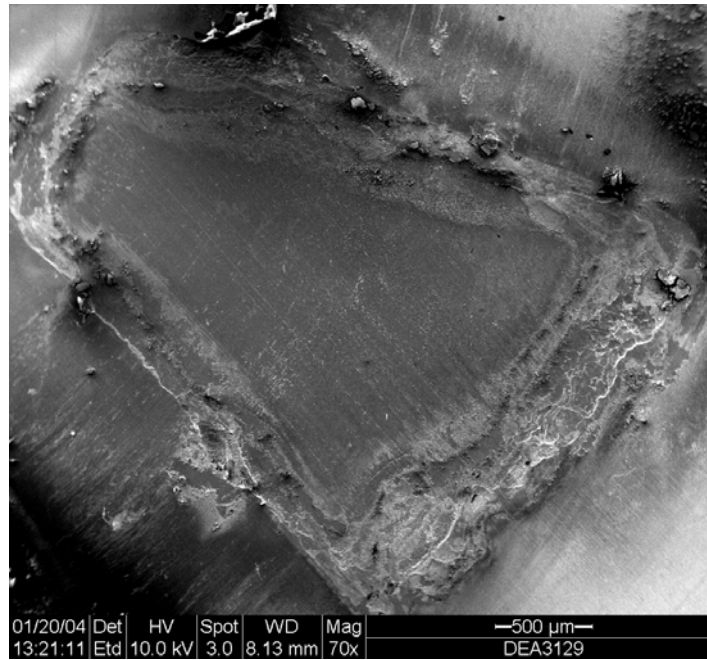of the temperature, effect of sulfate ions. Figure redrawn based on data from Ref. 26

FIGURE 7 – Crystalline appearance of Type I attack in Alloy 22.
Specimen DEA3129 tested using CPP in 1 M NaCl at 90°C. Magnification X70
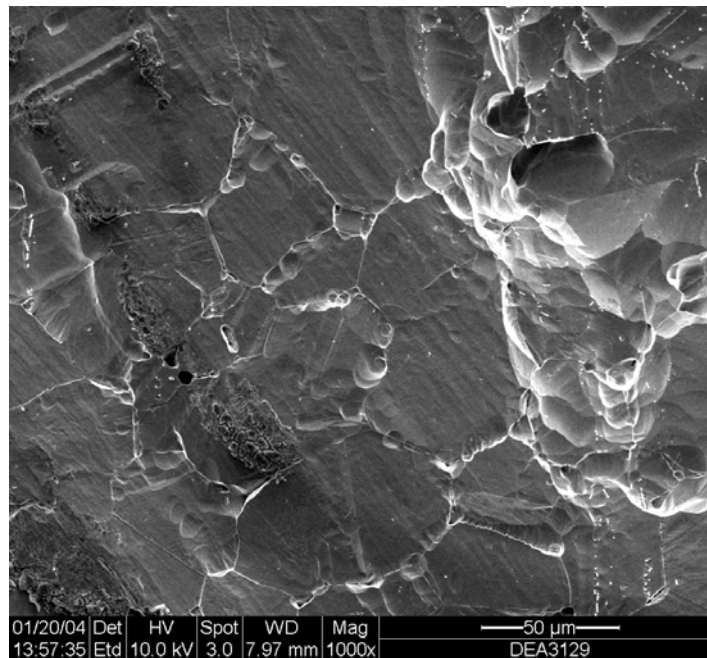


FIGURE 8 – Crystalline appearance of Type I attack in Alloy 22.
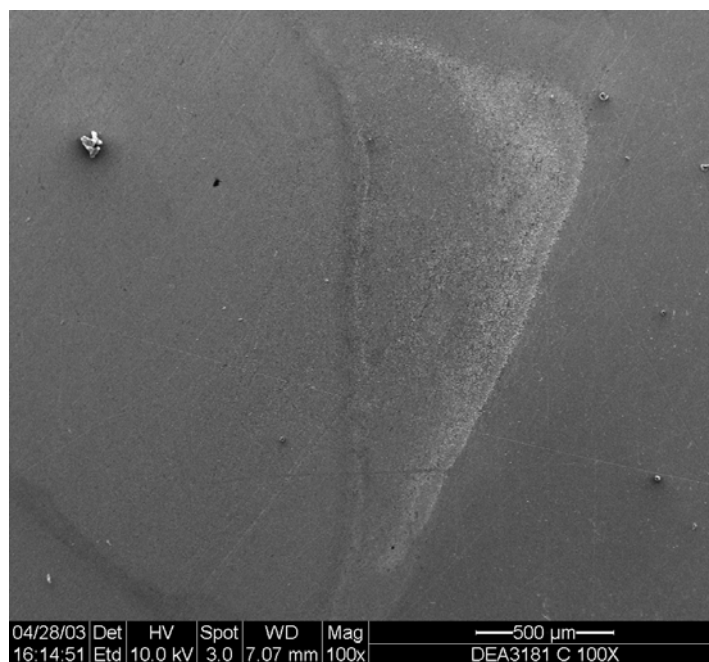Specimen DEA3129 tested using CPP in 1 M NaCl at 90°C. Magnification X1000

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FIGURE 9 – Type II of Attack in Alloy 22.
Specimen DEA3181 tested using CPP in 5 M CaCl$_2$ at 60°C. Magnification X100
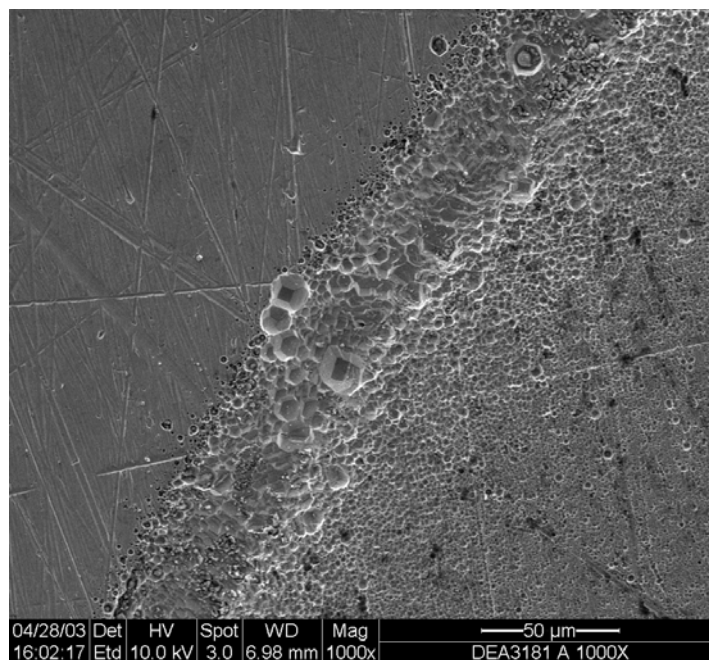


FIGURE 10 – Type II of Attack in Alloy 22. Small etch pits in the occluded area.
Specimen DEA3181 tested using CPP in 5 M CaCl$_2$ at 60°C. Magnification X1000